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LABORATORY STUDIES OF CHEMICAL AND PHOTOCHEMICAL PROCESSES RELEVANT TO STRATOSPHERIC OZONE

Prepared by

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1. RESEARCH OBJECTIVES

The purpose of this project is to reduce the uncertainty in several key gas-phase kinetic processes which impact our understanding of stratospheric ozone. The main emphasis of this work is on measuring rate coefficients and product channels for reactions of HO_x and NO_x species in the temperature range 200 K to 240 K relevant to the lower stratosphere. Other areas of study have included infrared spectroscopic studies of the HO_2 radical, measurements of OH radical reactions with alternative fluorocarbons, and determination of the vapor pressures of nitric acid hydrates under stratospheric conditions. The results of these studies will improve models of stratospheric ozone chemistry and predictions of perturbations due to human influences.

2. RESULTS FROM NASA SUPPORTED PROGRAM 1992-1995

Over the past three years we have focussed our efforts in three separate research areas: 1) spectroscopic and kinetic studies of the HO_2 radical, 2) the measurement of rate constants for the destruction of several potential alternative freon compounds by the OH radical and an assessment of the corresponding ozone depletion potentials and atmospheric lifetimes for these species, and 3) the determination of phase diagrams for nitric acid hydrates which are central to our understanding of the formation of polar stratospheric clouds. In addition, Dr. Kolb has participated in NASA's panel for Data Evaluation helping to prepare two versions of the JPL publication "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling". We shall discuss our work in each of these areas separately below.

2.1 Spectroscopy and Kinetics of the HO_2 Radical

HO_2 Quantitative Spectroscopy Studies

The hydroperoxyl radical (HO_2) participates in the formation and destruction of ozone in both the troposphere and the stratosphere. Together with the hydroxyl radical (OH) it forms catalytic cycles which result in the oxidation of compounds released at the surface of the earth and thus provides the major cleansing mechanism for hydrocarbons and manmade pollutants in the lower atmosphere. There is, therefore, great interest in direct measurements of the concentration and distribution of HO_2 radical throughout the atmosphere. Infrared spectroscopy provides a specific and sensitive method for detecting the HO_2 radical in laboratory studies and is a potential method for direct measurements in the stratosphere. We have augmented our previous work on line position and line strengths by measuring the pressure broadening coefficient in air for infrared transitions of HO_2 in the ν_2 vibrational band around 1400 cm^{-1}. This work has been published in the Journal of Molecular Spectroscopy [Nelson and Zahniser, 1994a].

The HO_2 was made at atmospheric pressure from the H + O_2 association reaction. The HO_2 was sampled by a fast flow reduced pressure multipass absorption cell using an astigmatic off axis resonator. The optical pathlength was 100 meters with 182 passes. A survey spectrum of HO_2 spanning 1410.9 to 1411.4 cm^{-1} is shown in the upper panel of Figure 1. An HO_2 resolved doublet, coincident doublet, and resolved quartet are seen with peak absorptions of ~2-5%. Also shown is the etalon trace used to calibrate the frequency scale for the pressure broadening measurements. The bottom panel of Figure 1 shows the result of a fit carried out on the spectrum

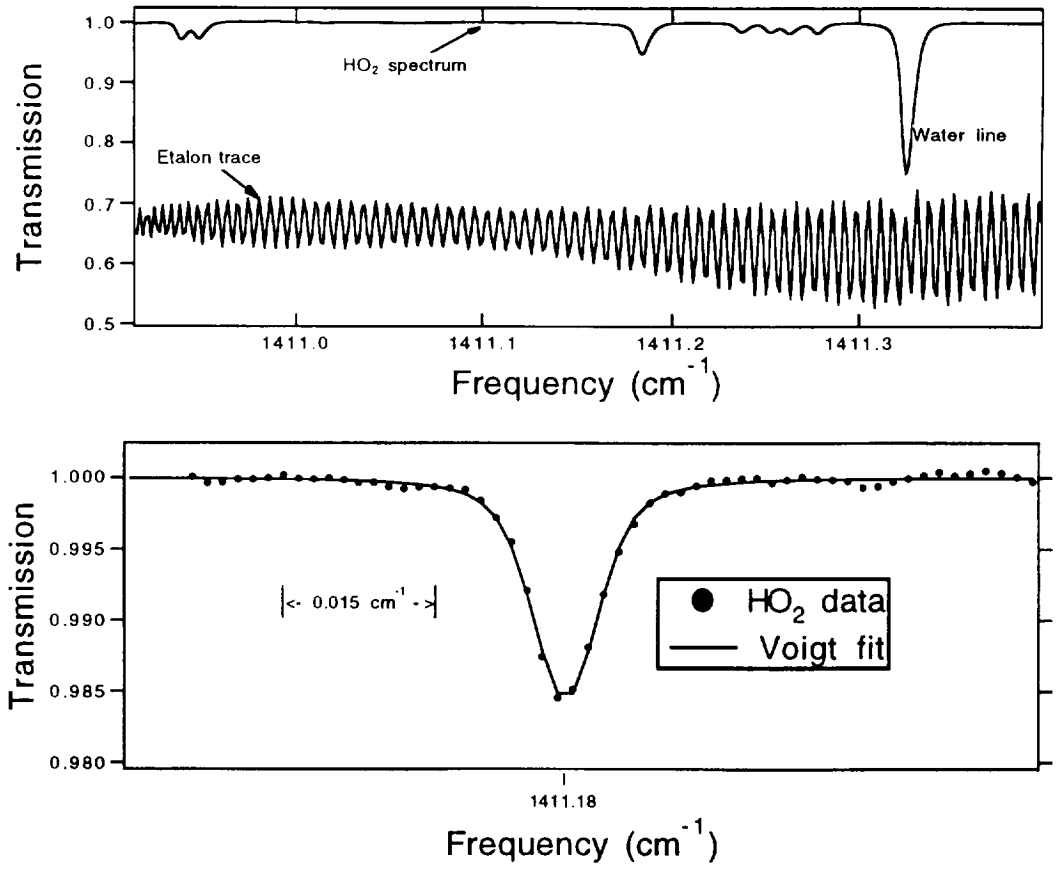

Figure 1. HO_2 Absorption Spectra Obtained in 100 Meter Pathlength Fast Response Flow Cell

of the coincident doublet ($9_{19} \leftarrow 8_{18}$ F_1,F_2) obtained at 16 Torr. Approximately 1/2 of the linewidth is Gaussian (due to Doppler and instrumental broadening) and ~1/2 is Lorentzian (due to pressure broadening). All of the broadening measurements reported in this work are based on this coincident doublet at 1411.18 cm^{-1}. The pressure was varied by throttling the pump. Spectra were taken at pressures from 5-80 Torr and fit to a Voigt profile using a nonlinear least squares fit as described above. In these fits the doublet was treated as a singlet since the two components of the doublet differ in frequency by only 0.0004 cm^{-1}. This splitting was completely unobservable even at low pressure, being dominated by the combined effects of Doppler broadening (Γ_{HWHM} = 0.0015 cm^{-1}) and the finite laser linewidth (Γ_{HWHM} ~ 0.0019 cm^{-1}). The laser linewidth appears to be largely Gaussian in nature and is deduced from the observed spectral linewidth (Γ_{HWHM} = 0.0024 cm^{-1}) at low pressure. This excess Gaussian broadening is attributed to the laser linewidth. The pressure dependent Voigt profiles were fit with the peak position, peak height

and Lorentzian halfwidth floated and the Gaussian halfwidth fixed at 0.0024 cm^{-1}. The reported pressure broadening coefficient is relatively insensitive to the value chosen for the Gaussian halfwidth.

Our results are summarized in Figure 2 where we plot the Lorentzian component of the observed linewidth versus the cell pressure both for room air and dry air. The error bars in Figure 2 are the 95% confidence limits derived from the random errors in the nonlinear least squares fits. Since there is no significant difference between the two data sets, they were fit together. This is not surprising since the water vapor mixing ratio in the cell was only 2.7 parts per thousand. The eleven observed halfwidths were fit to a straight line using a least squares fit weighted by the inverse of the plotted uncertainties. The slope of the fit line implies a broadening coefficient of 0.098 ± 0.007 cm^{-1} atm^{-1} (HWHM) for the gas mixture. The Lorentz halfwidth at zero pressure is determined as 0.0002 ± 0.0002 cm^{-1}. The reported uncertainties represent 95% confidence limits with respect to random errors. The mixture employed was 86.5% air, 13% He

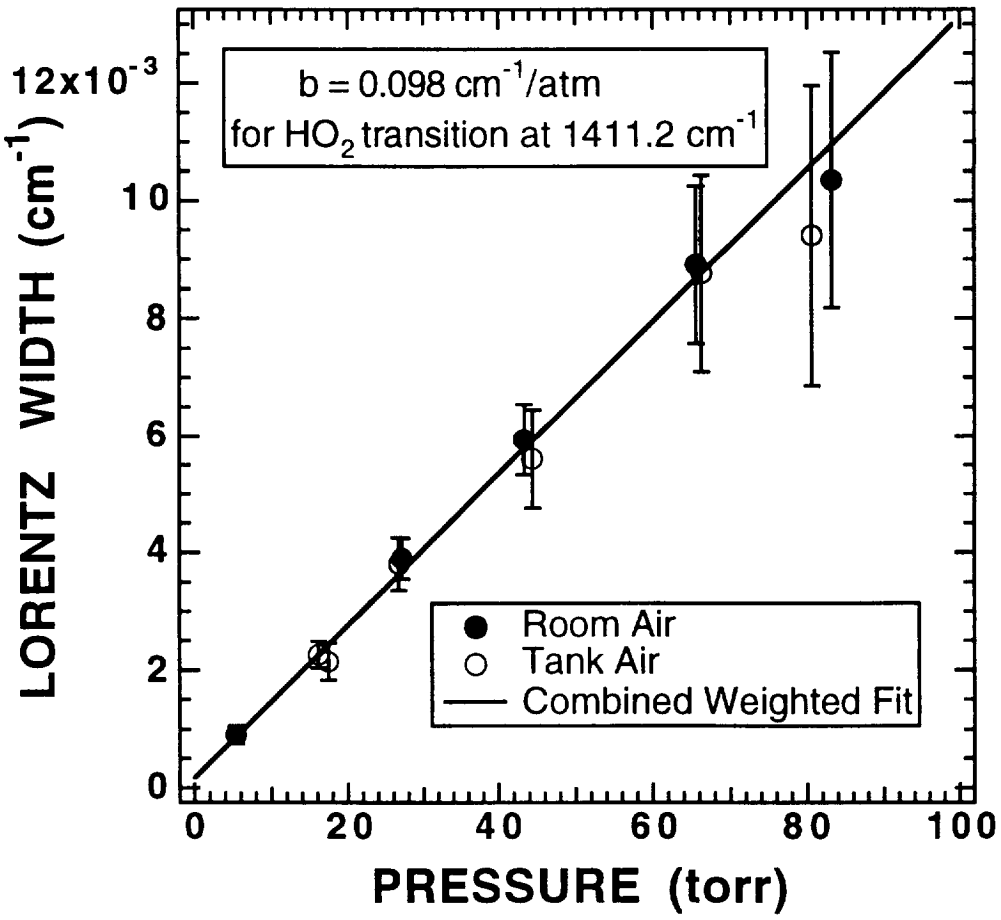

Figure 2. HO_2 Air Broadened Linewidth Measurements in a Mixture of 86.5% air, 13.5% Helium and 0.5% Hydrogen

and 0.5% H_2. It was difficult to vary this mixture substantially while maintaining sufficient HO_2 signal for pressure broadening studies. However, the He and H_2 concentrations were small enough that we can still report a fairly precise air broadening coefficient. We ignore the H_2 pressure broadening since H_2 is only present in trace quantities. To correct for the presence of He we note that the weakly interacting He atom is likely to be a much less efficient line broadener than either N_2 or O_2. In fact, the air broadening coefficients of OH rotational transitions are ~5x larger than the He broadening coefficients. We therefore assume that the He broadening coefficient with HO_2 is one third of the air broadening coefficient and we increase our reported uncertainties in the air broadening coefficients to allow for He broadening coefficients between 0 and 2/3 of the air broadening values. This implies an air broadening coefficient of 0.107 ±0.009 cm^{-1} atm^{-1} for the $9_{19} \leftarrow 8_{18}$ F_1,F_2 doublet (1411.180 cm^{-1}) in the ν_2 band.

The line broadening coefficient reported in this work has direct implications for the design and interpretation of atmospheric monitoring experiments for the hydroperoxyl radical. The two obvious implications are: 1) the broadening coefficient determines the maximum line center absorption for a given line strength, and 2) it determines the optimal pressure for reduced pressure sampling in the infrared absorption approach.

Further work on the HO_2 radical should certainly explore the rotational and vibrational dependence of the broadening coefficients. In addition, measurement of the temperature dependence of theses coefficients will be very important since lower stratospheric and upper tropospheric temperatures are often 200 K or lower. Direct monitoring of the HO_2 radical in these environments will potentially require a large temperature correction to the room temperature broadening coefficients.

<u>HO_2 Radical Reaction Kinetics</u>

The reaction of HO_2 with ozone is one of the most important ozone controlling reactions in the lower stratosphere. The precise determination of the rate of this reaction at temperatures characteristic of the lower stratosphere is therefore very important. The goal of our work in this area is to measure the rate of this reaction at temperatures approaching 190 K. Our measurement technique is the discharge flow method using fast sweep tunable diode lasers for detection of the HO_2 radicals in excess ozone. The study of this reaction is motivated by and complicated by the fact that it is part of a catalytic cycle which reforms HO_2 while eliminating ozone:

$$HO_2 + O_3 \rightarrow OH + 2\ O_2 \qquad (R1)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (R2)$$

$$\text{net:}\quad 2\ O_3 \rightarrow 3\ O_2$$

We have used isotopic labelling to prevent the second reaction from reforming the radical reactant of the first reaction. That is, we study the rate of $HQ_2 + O_3$ (where $Q = {}^{18}O$). HQ_2 is formed in an association reaction between H atoms and Q_2. The difficulty with this approach is that the reactants are quite expensive and an extra burden is placed on detection sensitivity. We have therefore overcome two major challenges in this study: 1) the difficulty of high radical wall losses at the colder temperatures and 2) the need for very high detection sensitivity.

Previous studies have been limited in their temperature range by severe HO_2 wall loss at temperatures below 240 K. Each of these studies employed either a CH_3OH source for HO_2 or a radical scavenger for the removal of OH or both. In this work, we have avoided using these condensible species and have had much less difficulty with radical wall loss, measuring wall loss rates as small as 6 s^{-1} at 219 K. We have also extended our detection limit for HO_2 radicals by a factor of ten by using a set of astigmatic off-axis resonator mirrors which provide a longer absorption path in a smaller sampling volume. We are currently using nearly 400 passes of the diode laser to detect the HO_2 radicals. With a high quality single mode laser this should translate to an HO_2 detection limit of ~2 x 10^8 molecules cm^{-3}. Unfortunately, we have had difficulty of late obtaining a high quality single mode HO_2 laser. We have made some kinetic measurements with a multimode laser at reduced sensitivity (detection limit ~ 10 x 10^8 molecules cm^{-3}). Our results to date are summarized in Figure 3, an Arrhenius plot for the HO_2 + ozone reaction. This plot shows our rate measurements together with those of previous workers. We have extended the temperature range of the rate measurements to almost 200 K, but the precision of the measurements is not yet good enough to distinguish between the linear Arrhenius plot of Zahniser and Howard [1980] (solid line) and the curved plot of Sinha, Lovejoy and Howard [1987] (dashed curve).

We are currently implementing three measures which will provide the sensitivity required to complete these experiments. First we are attempting to procure a single mode HO_2 laser from two sources. Second, we have ordered a pair of narrow bandwidth high reflective astigmatic mirrors which will allow ~720 passes of the infrared laser across the flow tube. We expect these two improvements to lower our HO_2 detection limit to ~ 1 x 10^8 molecules cm^{-3} in one minute. Third,

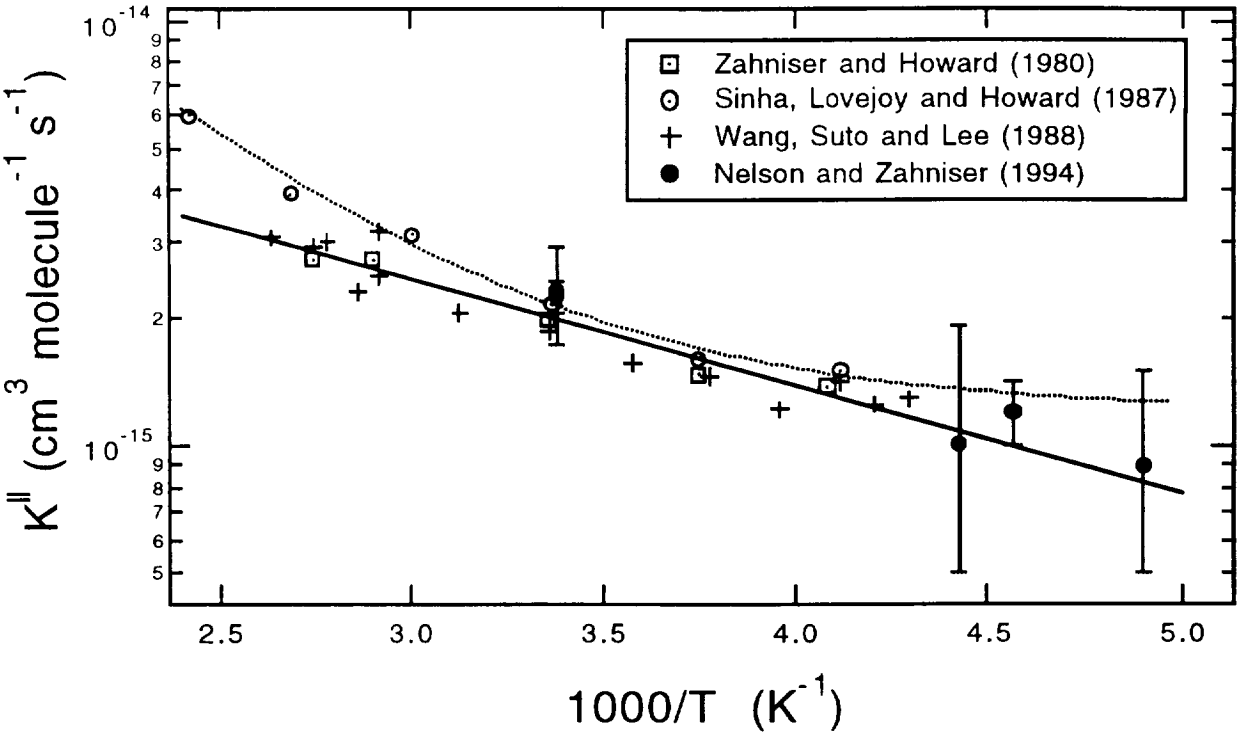

Figure 3. Arrhenius plot for the reaction of HO_2 radical with ozone.

we have ordered isotopically labelled HQQH which will be used to produce HQ_2 via F atom reaction. This source is far more efficient than the H + Q_2 source and thus produces HQ_2 at a substantially reduced cost allowing longer signal averaging. We have recently verified that this source works at stratospheric temperatures without introducing additional HO_2 wall loss. With these improvements nearly in place, we plan to complete the rate measurements in the next few months.

Another task performed under this contract was the preparation of an article for the Journal of Physical Chemistry [Nelson and Zahniser, 1994b] describing our measurements of the branching ratio of the HO_2 + ozone reaction. This article detailed work performed under a previous NASA contract. The study investigated the fraction of OH produced via hydrogen abstraction versus that produced via oxygen abstraction as a function of temperature. The conclusion of the work is that H atom abstraction is the dominant pathway from room temperature down to stratospheric temperatures and that variation in this aspect of the reaction mechanism does not account for the observed curvature in the HO_2 + O_3 Arrhenius plot.

The reaction of HO_2 + NO is also being studied using the discharge flow technique and infrared tunable diode laser absorption detection of HO_2. Concentrations of HO_2 are well below

the limit for interferences from second order processes. Our initial results, k(T = 294) = $(7.5 \pm 1.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and k(T = 263) = $(10.5 \pm 2.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, are in good agreement with previous measurements of Howard [1979].

2.2 OH Reaction Rates with Alternative Halocarbons

Hydrogen-containing halocarbons are being used as alternatives for fully halogenated compounds since their higher reactivity with OH radicals in the lower atmosphere limits their transport to the stratosphere and their resultant degradation of the ozone layer. The halons are widely used as fire extinguishers to exploit the effective combustion suppression observed with many bromine containing molecules. It is therefore important to develop alternatives for fire suppression which are less effective at delivering bromine to the stratosphere. The compounds studied in this work are examples of two distinct approaches to this problem. CF_3CFHCF_3 has been demonstrated as a fire fighting agent and since it contains no bromine or chlorine it is thought to pose no threat to stratospheric ozone. Unfortunately, CF_3CFHCF_3 is not an ideal fire suppressant [Baldwin et al., 1992] since it is less efficient than the halons and has a propensity to produce undesirable quantities of HF when applied to fires. In addition, CF_3CFHCF_3 is a potential greenhouse gas whose release could contribute to global warming. The second approach to fire suppression alternatives is exemplified by CF_3CH_2Br. Hydrogenated halons such as CF_3CH_2Br contain both bromine atoms capable of fire suppression and hydrogen atoms allowing the efficient tropospheric removal of the parent compound. However, with the high efficiency of bromine catalyzed ozone destruction, tropospheric lifetimes on the order of a few months will likely be necessary to permit the widespread use of these compounds.

The second order rate constants for each reaction are displayed in Figure 4 as a function of temperature, where we have plotted ln (k^{II}) versus 1/T. These Arrhenius plots are linear, indicating that the temperature dependent rate constants are well represented by:

$$k^{II} = A \exp [-E / (R T)] \qquad (1)$$

Weighted linear least squares fits of ln (k^{II}) versus 1 / T were used to determine A and E. We report $A = (3.7 \pm 1.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} and $E/R = 1615 \pm 190$ K for $OH + CF_3CFHCF_3$ and $A = (1.39 \pm 0.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and $E/R = 1350 \pm 195$ K for $OH + CF_3CH_2Br$. The random error uncertainties in A and E were estimated from the deviation of the k^{II} values from the fit. These uncertainties were convolved with a 10% systematic error uncertainty to yield the total reported uncertainties in A and E with a ~95% confidence limit. The uncertainty in k^{II} as calculated from Eq. (1) is estimated to be ~10% over the measured temperature range. The

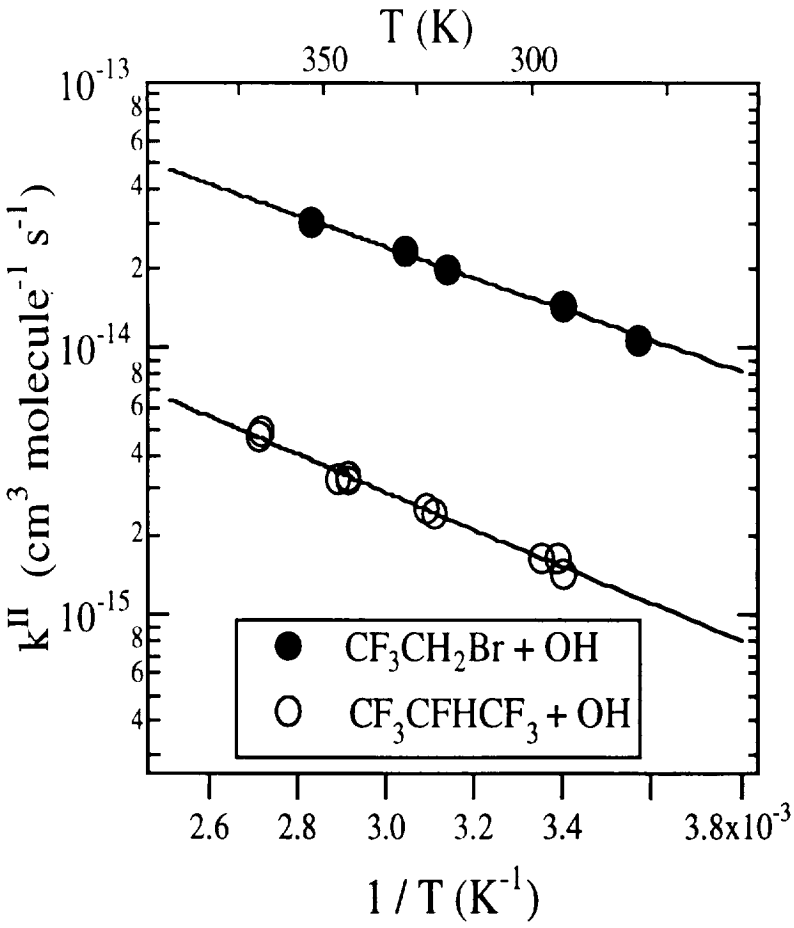

Figure 4. Arrhenious plots for the reactions of CF_3CFHCF_3 and CF_3CH_2Br with the OH radical.

uncertainty in k^{II} over the wider range of T = 250 - 400 K is conservatively reported as less than or equal to 20%. This estimate is based upon the uncertainty in our determination of E.

The temperature dependent rate constants measured in this work are required to calculate the tropospheric lifetimes of CF_3CFHCF_3 and CF_3CH_2Br with respect to removal by reaction with OH radical. Following the approach of Prather and Spivakovsky [1990], we use the OH rate constants at 277 K to estimate lifetimes. The tropospheric lifetimes, τ_x, are calculated from the OH reaction rates, k_x, via the simple procedure of scaling from the methyl chloroform tropospheric lifetime of Prinn et al. [1995] and the OH reaction rate constant [Talukdar et al., 1992] .The resulting tropospheric lifetimes (with respect to OH reaction) for CF_3CFHCF_3 and CF_3CH_2Br are 42 years and 4.4 years, respectively.

For both compounds studied in this work, the atmospheric lifetimes will be nearly equal to the tropospheric lifetimes, most likely within 10%. We expect photolysis and $O(^1D)$ lifetimes of many, many centuries for CF_3CFHCF_3 and we estimate an atmospheric lifetime equal to its tropospheric lifetime of 42 years. For CF_3CH_2Br, the tropospheric lifetime is so short that only a very rapid stratospheric process could significantly affect the atmospheric lifetime. Photolysis is the only obvious possibility. We expect the stratospheric lifetime of CF_3CH_2Br with respect to photolysis to be roughly equal to the stratospheric lifetime of CF_3Br (65 years, [Burkholder et al., 1991]). This implies an atmospheric lifetime of 4.1 years for CF_3CH_2Br.

The steady state ozone depletion potential (ODP) for CF_3CH_2Br can be estimated from its atmospheric lifetime following the empirical approach of Solomon et al. [1992]. The steady state globally averaged ozone depletion potential for a halon compound may be calculated as:

$$ODP = (\tau_x / \tau_{CFC\text{-}11}) \times (M_{CFC\text{-}11} / M_x) \times (k_x / 3) \times \alpha \qquad (2)$$

where τ_x is the atmospheric lifetime of the halon, $\tau_{CFC\text{-}11}$ is the atmospheric lifetime of CFC-11 (taken as 55 years [WMO, 1991]), M_x and $M_{CFC\text{-}11}$ are the molecular weights of the species, k_x is the number of Br atoms in the halon and α is an efficiency factor which quantifies the relative effectiveness for ozone destruction of free bromine compared to free chlorine. The parameter α is a function of altitude and the free chlorine concentration. A value of 40 has been recommended as a global average [WMO, 1991] and is used here. It should be noted that this factor is quite uncertain and applies in an average sense to the present polar stratosphere. The resulting ozone depletion potential for CF_3CH_2Br is 0.84 with an overall uncertainty of approximately a factor of two. This ODP is far smaller than those of halon-1301 (ODP ~16) and halon-1211 (ODP ~4), [WMO, 1991] which have been used widely as fire suppression agents. This work is published in Geophysical Research Letters [Nelson et al., 1993].

In addition to the alternative halon work described above, we have recently completed a series of OH reactions with several HFC species. Room temperature reaction rates with OH were measured for six fluoropropanes, one fluorobutane and one fluoropentane. High purity samples of these species were provided by Allied Signal Corp. who also partially sponsored this work. The room temperature reaction rates for these species are presented in Table 1. The uncertainties in these values are typically 10-15% including potential systematic errors. The measured reaction rates vary by a factor of ~100 and show the dramatic deactivation associated with F substitution. In addition, the temperature dependence for the reaction of OH with $CF_3CH_2CF_2CH_2CF_3$ was measured by measuring k at 5 temperatures between 278 and 354 K. The data is fit well by an Arrhenius expression with $A = (1.28 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R = 1833 \pm 250$ K.

A manuscript describing our measurement of these and OH reaction rates has been published recently [Nelson et al., 1995].

Table 1 - OH Room Temperature Reaction Rates with Several HFC's

HFC	K_{exp} x 10^{15} (cm^3 $molecule^{-1}$ s^{-1})
CHF_2 CHF CHF_2	16.0
CF_3 CH_2 CF_3	0.57
CF_3 CH_2 CH_3	42.
CF_3 CHF CHF_2	5.3
CF_3 CH_2 CHF_2	6.6
CF_3 CHF CH_2F	14.8
CF_3 CH_2 CH_2 CF_3	7.0
CF_3 CH_2 CF_2 CH_2 CF_3	2.62

2.3 Thermodynamic Studies of Nitric Acid Hydrates at Stratospheric Temperatures

The importance of heterogeneous chemical reactions on stratospheric aerosol surfaces has been vividly demonstrated by measurements and models of the polar stratosphere. We have determined the thermodynamic parameters for nitric acid mono-, di-, and tri- hydrates by vapor pressure measurements of water and nitric acid in equilibrium with the solid phases using tunable diode laser spectroscopy. Our experiments indicate that nucleation and persistence of the metastable $HNO_3 \cdot 2H_2O$ may be favored in polar stratospheric cloud over $HNO_3 \cdot 3H_2O$ even though the later is thermodynamically more stable under typical stratospheric conditions of temperature, water vapor and nitric acid vapor. The nitric acid hydrate studies are being conducted in collaboration with S. Wofsy and L. Fox from Harvard University. The results of this initial study have been published in Science [Worsnop et al., 1993].

We have continued these studies of nitric acid hydrates relevant to polar stratospheric cloud formation by investigating mixtures with sulfuric acid. Formation of crystalline phases of H_2SO_4, HNO_3 and H_2O were studied at stratospheric temperatures and vapor pressures. Freezing of

supercooled solutions began at < 200 K by crystallization of $x \cdot H_2SO_4 \cdot HNO_3 \cdot H_2O$, where x is presently undetermined, followed by a progression of metastable phases: [$H_2SO_4 \cdot H_2O$ + $x \cdot H_2SO_4 \cdot HNO_3 \cdot H_2O$ + solution] →(fast) [$H_2SO_4 \cdot 4H_2O$ + $H_2SO_4 \cdot 6.5H_2O$ + $HNO_3 \cdot 2H_2O$] →(slow) [$H_2SO_4 \cdot 4H_2O$ + $H_2SO_4 \cdot 6.5H_2O$ + $HNO_3 \cdot 3H_2O$]. Metastable $HNO_3 \cdot 3H_2O$ formed in some experiments. Large particles are readily produced from metastable phases, providing a mechanism for removal of HNO_3. Mixed crystals partially melted at 200 K, forming [$H_2SO_4 \cdot 4H_2O$ + ternary solution], a potentially important process in the arctic polar vortex.

This work has been partially funded by the NASA High Speed Research Program and the National Science Foundation in addition to the NASA Upper Atmospheric Research Program. A publication detailing this work has appeared in Science [Fox et al., 1995].

2.4 NASA Data Evaluation Panel Activity

During our current contract C.E. Kolb has served on NASA's Panel for Data Evaluation as the panel's lead member responsible for heterogeneous processes. Due to his efforts the Heterogeneous Chemistry section of the biennial review, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, first introduced in 1990, has been completely revised and significantly expanded in both the tenth [DeMore et al, 1992] and eleventh [DeMore et al., 1994] editions. The Heterogeneous Chemistry section now includes three data tables covering Mass Accommodation Coefficients, Gas/Surface Reaction Probabilities, and Henry's Law Constants for Gas-Liquid Solubilities, as well as text and extensive notes presenting background and guidance for using the tables. The eleventh edition of the Heterogeneous Chemistry section presents and evaluates the work for over eighty new or revised archival publications beyond the tenth edition.

2.5 Archival Publications Prepared Under the Current Contract

D.R. Worsnop, L.E. Fox, M.S. Zahniser, and S.C. Wofsy, "Vapor Pressures of Solid Hydrates of Nitric Acid: Implications of Polar Stratospheric Clouds", Science 259, 71 (1993).

D.D. Nelson, M.S. Zahniser and C.E. Kolb, "OH Reaction Kinetics and Atmospheric Lifetimes of CF_3CFHCF_3 and CF_3CH_2Br", Geophys. Res. Letters 20, 197 (1993).

D.D. Nelson and M.S. Zahniser, "A Mechanistic Study of the Reaction of HO_2 Radical with Ozone", J. Phys. Chem. 98, 2101 (1994a).

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